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Association of Cations with Anionic Polyelectrolytes in Dilute Solution

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The intrinsic viscosity determination on a sample of carboxymethyl cellulose was made for the aqueous solutions at the presence of simple electrolytes. The argument deduced from the data suggested that a certain fraction of the counter-ion associates with the polyelectrolyte molecule and the stoichiometric number of ionizable groups on the polyion, Z , ceases to be an effective quantity by which some electrolytic properties of the system may be determined. An "effective number of ionizable groups" (say Z^*) was defined, and was evaluated according to Pals and Hermans' procedure in connection with Flory's equation for the intrinsic viscosity of neutral polymer. It was thus found that the ratio Z/Z^* is always smaller than unity even for the 1-1 electrolytes added and tends to decrease rapidly with increase in the valency of cation. This fact was interpreted in terms of the association of cations with anionic polyelectrolytes.

INTRODUCTION

Recent investigations on linear polyelectrolytes¹⁻³⁾ have suggested that a certain fraction of counter ions of polyelectrolytes in dilute solution is bound in or on a macromolecular domain over which the polyion extends in a time average. This binding of counter ions to polyelectrolyte molecules reduces the depth of the potential well produced by high charges of the polyion, and makes the stoichiometric number of electric charges on the polyion cease to be an important quantity that electrolytic properties of the solution may thereby be determined. This idea has been treated theoretically by Oosawa *et al.*⁴⁾ who solved Poisson-Boltzmann's equation without introduction of Debye-Hückel's approximation.

The present work deals with viscosities of the polyelectrolyte in various media involving different electrolytes. It is shown how the theories based on the assumption of complete dissociation of the polyelectrolyte molecule can be applied to the analysis of experimental data for the viscosity of dilute polyelectrolyte solutions. A commercial product of sodium carboxymethyl cellulose (Na-CMC) was taken as the sample for this study, and its viscosities in water were measured in the presence of several kinds of simple electrolytes. The intrinsic viscosities were expressed as a function of simple electrolyte content and analyzed according to the procedure of Pals and Hermans⁵⁾ which is based on the theory of Hermans and Overbeek⁶⁾ on

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dilute solutions of linear polyelectrolytes. As a result of this analysis, it was found that, if the number of electric charges on the polyion is treated as a stoichiometric quantity, an irrational conclusion must be drawn out. It is shown, however, that this difficulty can be eliminated by introducing for Z in Pals and Hermans' treatment a quantity "effective charge" of the polyion which is smaller in number than the stoichiometric charge. This fact is attributed to the association of cations with anionic polyelectrolyte molecules.

EXPERIMENTAL

Material

The sample used in this work was a commercial sodium carboxymethyl cellulose which was designated as "Premium Low Viscosity Type". To purify the sample the material was shaken with a mixture of one part of water and nine parts of methanol, allowed to stand for 10 hours at about 50°C. and filtered. This procedure was repeated until the filtrate was entirely freed from the chlorine ion, which was confirmed by the silver nitrate test. The purified material was dissolved into a mixture of seven parts of water and three parts of ethanol at about 1.5 per cent polymer concentration and was precipitated using 98 per cent ethanol as precipitant. The degree of substitution of the polymer salt thus obtained was found to be 0.73 by means of the conductometric titration, and also checked by the ash content.

The simple electrolytes used were the materials which had been purified according to the procedure relevant to each. The water employed as solvent in this study was distilled two times in the presence of potassium permanganate and caustic soda, using a quartz tube.

Measurement of Viscosity

One of the difficulties encountered in accurate measurements of the viscosity of polyelectrolyte solutions is the elimination of shear-rate effect. It is well known that, when the content of an extraneous electrolyte is very low, the viscosity of polyelectrolyte solution is markedly affected by shear-rate even at very low concentrations, and that this effect diminishes with increasing amount of added electrolyte⁷⁾. A number of usual Ostwald-type viscometers each of which had a reservoir of approximately equal volume and had a capillary tube of different radius were prepared and selectively used so that efflux time of a give solution might be in a range from 420 to 450 sec. In this way, viscosities of solutions tested in this work could be compared at almost the same shear-rates. Corrections for kinetic energy, drainage and surface tension were found to be negligible in all cases examined. The measurement were conducted at $25.00 \pm 0.01^\circ\text{C}$.

RESULTS AND DISCUSSION

Reduced viscosities of polymer solutions are plotted against concentrations of polymer for several electrolytes in Figure 1. The intrinsic viscosity in each case was evaluated graphically from this figure and is listed in Table 1. It is seen from the figure that viscosity curves can be extrapolated in the usual manner to zero concentration of polymer when the content of added electrolyte is sufficiently large but for curves which have a maximum the values of intrinsic viscosity have to be determined

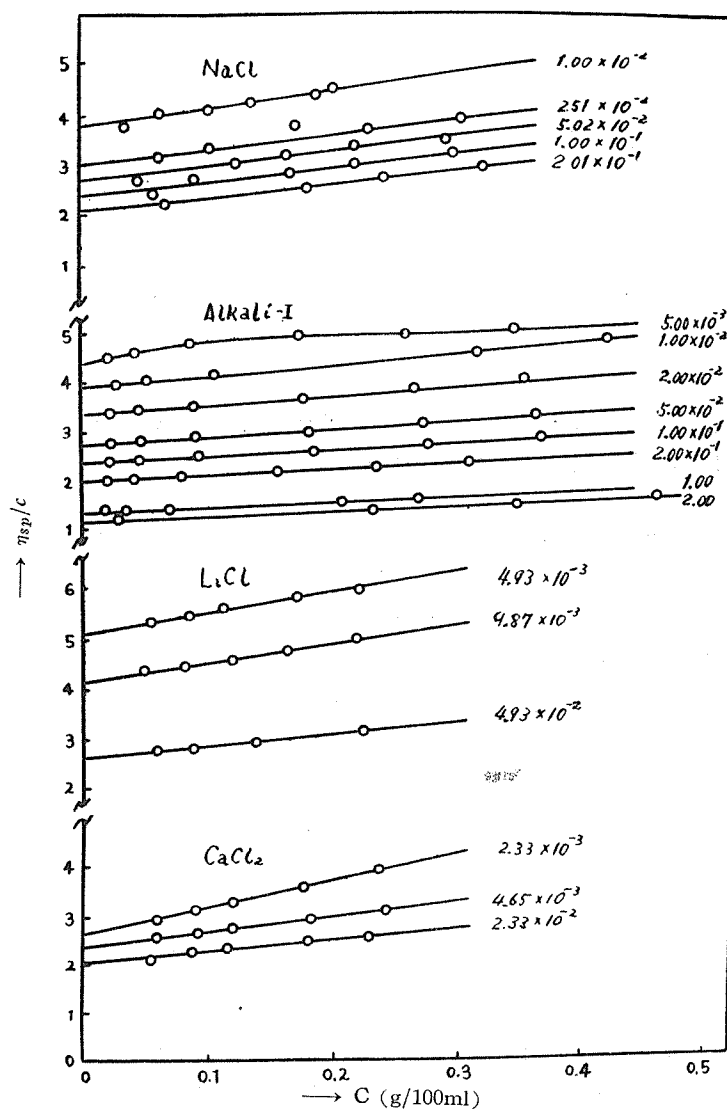


Fig. 1. Relations between reduced viscosity and concentration.

Table 1. Intrinsic viscosities for different electrolyte contents and different sorts of electrolyte.

Added simple electrolytes	concentration 10^2x (moles/l)	$[\eta]$	Added simple electrolytes	concentration 10^2x (moles/l)	$[\eta]$
NaCl	1.00	3.86	Na_2CO_3	0.200	5.11
	2.51	3.11		0.495	3.84
	5.02	2.65		0.990	3.46
	10.0	2.33		1.98	2.83
	20.1	2.13		4.95	2.28
Alkali-I NaOH: 44.2 % Na_2CO_3 : 7.8 %	1.00	3.85	Na_3PO_4	0.155	5.02
	2.00	3.33		0.310	4.13
	5.20	2.72		0.465	3.64
	10.0	2.35		0.620	3.47
	20.0	1.98	LiCl	0.493	5.18
100	100	1.33		0.987	4.16
	200	1.19		4.93	2.63
Alkali-II NaOH: 44.2 % Na_2CO_3 : 55.8 %	1.00	3.55	MgCl_2	0.101	3.82
	2.00	3.03		0.135	3.42
	5.00	2.46		0.253	2.86
	10.0	2.13		0.507	2.53
	20.0	1.96		1.01	2.27
100	100	1.63	CaCl_2	0.233	2.56
				0.465	2.31
				2.33	1.93

by extrapolating a linear part on the left side of the maximum. The iso-ionic dilution method⁸⁾ for evaluating the intrinsic viscosity was not employed in the present work.

The value of intrinsic viscosity, $[\eta]_\infty$, as a function of ionic strength, x , of the solution may be analyzed according to the procedure developed by Pals and Hermans⁵⁾. They have shown that the intrinsic viscosity *versus* $(x)^{-1/2}$ relation can be approximated in a region of high enough value of x by a straight line:

$$[\eta] = [\eta]_\infty' + B' (10^3 x)^{-\frac{1}{2}} \quad (1)$$

where

$$[\eta]_\infty' = \frac{1.55}{2} [\eta]_\infty, \quad (2)$$

$$B' = \frac{[\eta]_\infty'}{1.55} B \quad (3)$$

and

$$B = 570 N^{-\frac{1}{2}} Z (Pb^2)^{-\frac{3}{4}} \quad (4)$$

Here $[\eta]_\infty$ = intrinsic viscosity for sufficiently large x (*i. e.*, for the case where the polyion is completely discharged), N = Avogadro's number, Z = number of ionizable groups on macromolecule, P = degree of polymerization, and b = effective bond length for polyion discharged completely.

Association of Cations with Polyelectrolytes

It is to be noticed that systematic results can be obtained only when an ionic strength for cations only is correlated to the intrinsic viscosities. If, on the other hand, the usual ionic strength x is used, slope of the plot is different for different electrolytes of the same type as shown in Figure 2. The ionic strength for cations is defined by

$$I_s = \sum_i \nu_i z_i^2 m_i, \quad (5)$$

where ν_i is the number of cation in a molecule of the i -th electrolyte, z_i is the valency of that cation, and m_i is the concentration in moles/liter, and the summation is extended over cations only. (The usual factor $1/2$ should be dropped.) The reason why the ionic strength for cations only was used bases on the assumption that cations predominantly influence the electrolytic features of anionic polyelectrolytes.

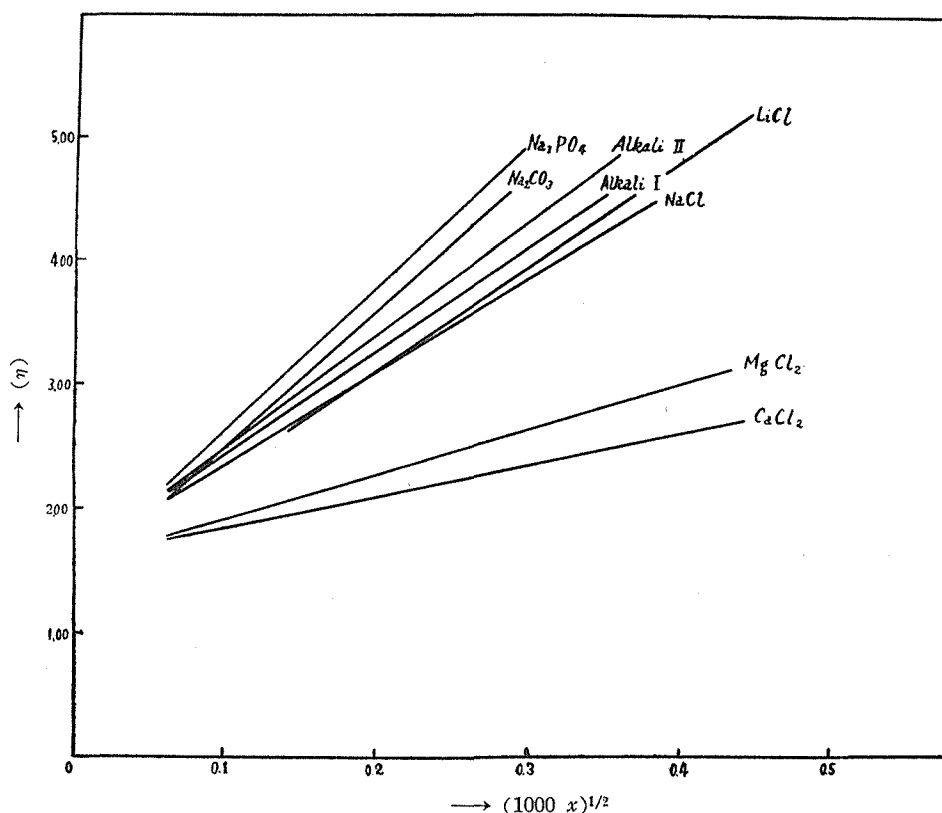


Fig. 2. Intrinsic viscosity as a function of usual ionic strength.

Figure 3 shows the plots of $[\eta]_\infty$ against $(I_s)^{-1/2}$. It can be seen from the figure that the plots of all the electrolytes having univalent cations coincide and can be expressed by a single line. However, the curves for magnesium chloride and calcium chloride, which have divalent cations, differs from the curve for electrolytes comprising univalent cations.

The values of $[\eta]_\infty$ and B calculated from Equations 2 and 3 using the results

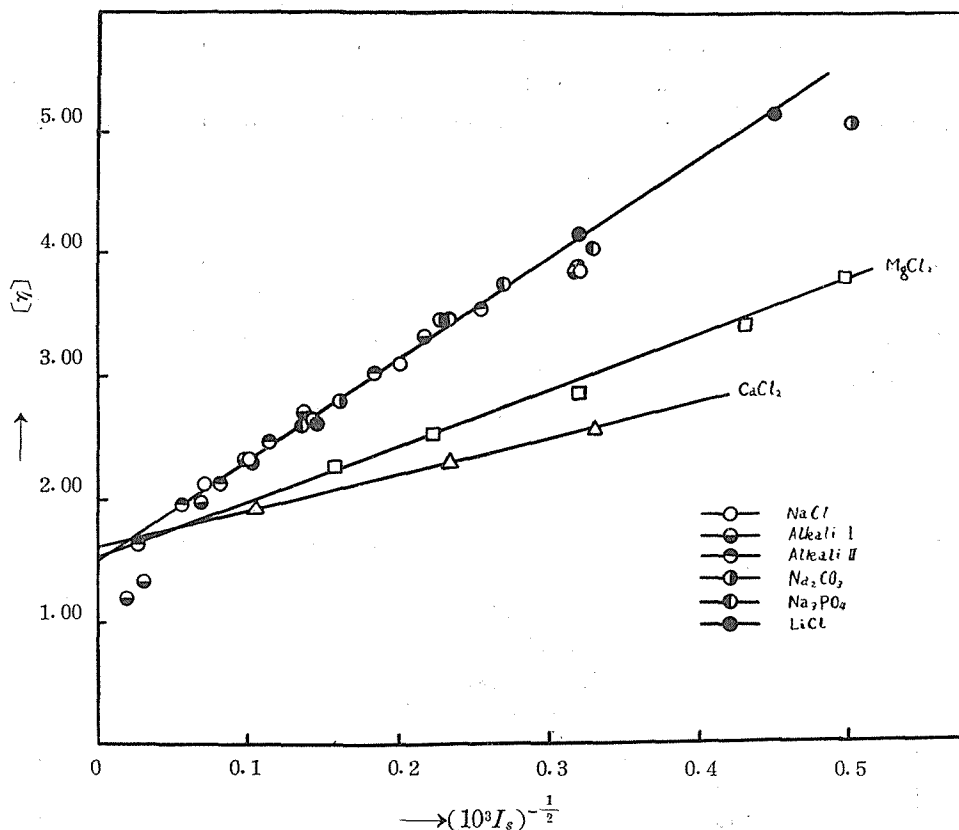


Fig. 3. Intrinsic viscosity as a function of ionic strength for cation only, I_s .

shown in Figure 3 are summarized in Table 2. It is seen from the table that the values of $[\eta]_\infty$ for all simple electrolytes studied here are equal within experimental error, while the values of B are markedly different for different electrolytes. The former fact suggests that by-ions, *i. e.*, Cl⁻ and OH⁻ ions in the present case, affect little the molecular dimension of the polyion at sufficiently high ionic strengths of the solution. This may be expected because anions are expelled away from the environment of the anionic polyion. That B depends markedly on the sort of electrolytes added seems to be contradictory, because, as can be inferred from Equation 4, B is a measure of the effective bond-length b which should be independent of the sort or valency of added electrolytes. In fact, if the number of ionizable groups on the polyion is a given quantity for a given polyelectrolyte, the above results obtained for B , particularly with magnesium chloride and calcium chloride, lead to the conclusion that the b value varies with the sort or valency of electrolyte added.

Before proceeding to considering this confusion, we calculate the b value for our own polyelectrolyte sample using experimental B and $[\eta]_\infty$ values. Referring to Pals and Hermans' data for a sample of Na-CMC (No. 74) whose number of equivalents

per gram of polymer salt, r , is equal to that of ours, the degree of polymerization (DP) of our sample is estimated to be 175. From these values Z is computed to be 128. Using this value of Z , b is calculated from Equation 4 as follows: $b=38\text{\AA}$, for electrolytes having univalent cations. This value agrees with those obtained by Pals and Hermans and others.⁹⁾ On the other hand, if we assume that the present polyelectrolyte molecule behaves like a neutral polymer at the limit of infinite I_s , we may apply Flory's equation for the intrinsic viscosity¹⁰⁾ to the $[\eta]_\infty$ value in the form

$$[\eta] = \phi(\bar{h}^2)^{3/2}/M, \quad (6)$$

where ϕ is Flory's universal constant relating the intrinsic viscosity to the molecular dimension $(\bar{h}^2)^{1/2}$ and molecular weight M . Putting $[\eta]=1.98$, $\phi=2.1\times 10^{21}$ and $M=39,000$, $(\bar{h}^2)=1.1\times 10^{-11}$ is obtained from Equation 6. Considering that the length of kinetic unit for the chain of cellulose derivatives is within a range of 110–180 \AA , as was suggested by Kuhn *et al.*,¹¹⁾ the b value of 38 \AA seems to be too large, and the value 25 \AA from Flory's equation appears to be more reasonable.

The confusion mentioned above as to the dependence of b on added electrolyte may be avoided if we keep the b value independent of the sort of extraneous electrolytes and instead treat the Z -value in Equation 4 as a variable parameter which depends on the state of counter ions in and around the molecular domain of the polyion. The Z value, regarded now as a parameter not specific for a given polyelectrolyte, may be called the effective number of ionizable groups and can be computed from Equation 4 with $b=25\text{\AA}$ for each added electrolyte. The values obtained are listed in the fifth column of Table 2 with a heading Z^* .

Table 2.

	B	$[\eta]_\infty$	Z	Z^*	Z^*/Z
Electrolytes involving univalent cations	8.31	1.96	128	52	0.40
MgCl ₂	4.36	2.00	—	27	0.24
CaCl ₂	2.28	2.08	—	18	0.14

It is seen from the table that Z^* values are remarkably lower than the stoichiometric number of ionizable groups, Z , for all the cases examined here and are dependent on the valency of cation. In the cases of divalent cations, the Z^* value is further dependent on the sort of cation. An explanation of why the Z^* value for the univalent cations differs from those for the divalent cations, may be obtained if we assume that divalent cations are associated with the polyion not only by the ionic interaction but also by a binding of chemical nature. The fact that the Z^* value for Ca-ion is smaller than that for Mg-ion may be considered in connection with the solubilities

of organic salts such as calcium oxalate and magnesium oxalate.

A physical significance of Z^* has recently been shown in measuring osmotic pressures of this system. It was found that the observed slopes of reduced osmotic pressure *versus* concentration closely approach those expected from the theory of the Donnan equilibrium^{12,13)} when the theoretical magnitude of the slope is multiplied by a factor $(Z^*/Z)^2$. The result on this subject will be published in near future.

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